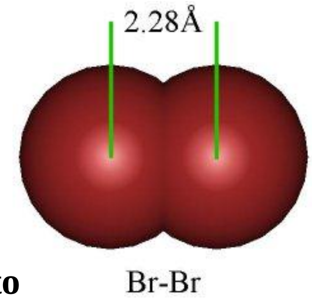
Inorganic chemistry

Lecturer . 6

Periodic Properties of the Elements

Three properties that provide important insights into chemical behavior include:

1. **atomic size**
2. **ionization energy**
3. **electron affinity**



Size of atoms

From the quantum mechanical model of atoms we can reaches to

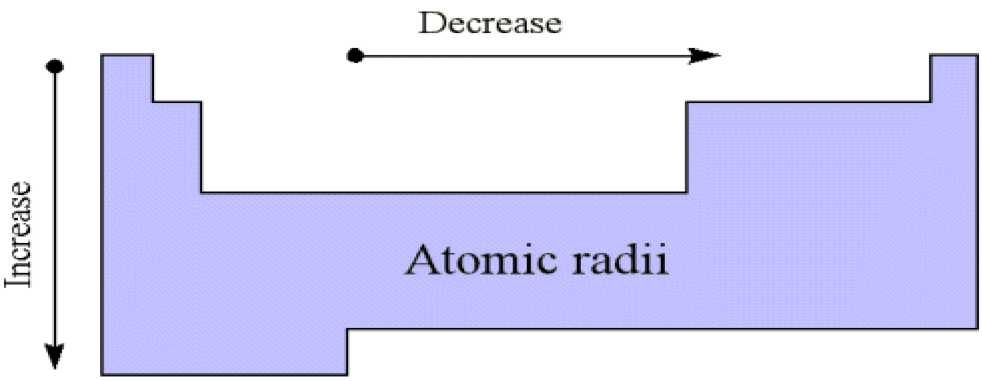
what exactly is the "size" of an atom?

- **The Br-Br distance in Br_2 is 2.28 Å, thus the radius of the Br atom is 1.14 Å**
- **The C-C bond distance is 1.54 Å, thus the radius of Carbon is 0.77 Å**

What are the general characteristics of atomic bond lengths ?

as determined from bond-bond distances (small molecule crystallography, NMR, other methods)

- **Within the *columns* of the periodic table, the atomic *radii increase as you go down the column***
- **Within the *rows* of the periodic table, the atomic radii *decrease as you move to the right***

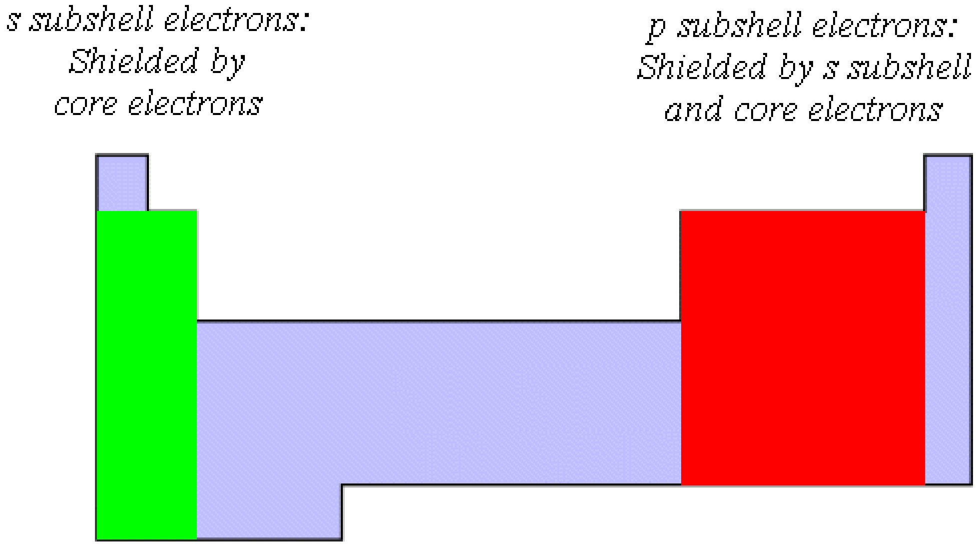


General trends for elements filling the *s* and *p* orbitals

What is the basis for these observations?

Two general factors affect the size of the outermost orbital:

- **The principle quantum number**
- **The effective nuclear charge**



Ionization Energy

The *ionization energy* of an atom measures *how strongly an atom holds its electrons*

The ionization energy is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom

Note that this does not mean the energy required to remove an electron from the *n*=1 shell (i.e the ground state orbital), the ground state here refers to the lowest energy electron configuration for the element in question

The *first ionization energy, I_1*, is the energy needed to remove the first electron from the atom:

$$Na(g) \rightarrow Na^+(g) + 1e^-$$

The *second ionization energy, I_2*, is the energy needed to remove the next (i.e. the second) electron from the atom

$$Na^+(g) \rightarrow Na^{2+}(g) + 1e^-$$

The *higher* the value of the ionization energy, the more *difficult* it is to remove the electron

Ionization energies (kJ/mol)				
Element	**I_1**	**I_2**	**I_3**	**I_4**
Na	**496**	**4560**		
Mg	**738**	**1450**	**7730**	
Al	**577**	**1816**	**2744**	**11,600**

- **There is also a big increase in ionization energy for removal of an electron from an inner shell (lower *n* value).**
  This is due to the fact that when you move to an orbital with a lower principle quantum number, you are removing an electron which is much closer to the nucleus (and has a higher attraction for the nucleus)
  The inner shell electrons are too tightly bound to be ionized or shared with another atom, and thus do not participate in chemical bonding

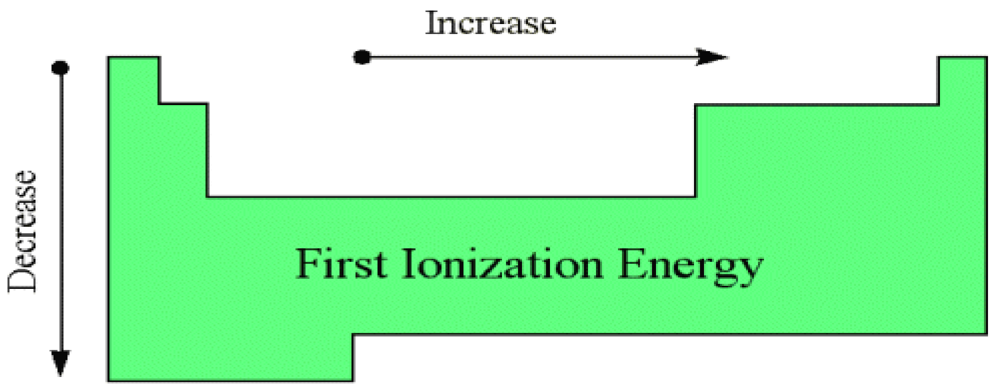
As electrons are removed, the positive charge from the nucleus remains unchanged, however, there is less repulsion between the remaining electrons

- **Z_{eff} increases with removal of electrons**
- **Greater energy is needed to remove remaining electrons (i.e. *the ionization energy is higher for each subsequent electron*)**

<u>Periodic trends in ionization energies</u>

First ionization energies as a function of atomic number

- **Within each period (row) the ionization energy typically increases with atomic number**
- **Within each group (column) the ionization energy typically decreases with increasing atomic number**



General trends for the energy required to remove the first electron (first ionization energy) of an element

The basis for these observations:

- **As the effective charge increases, or as the distance of the electron from the nucleus decreases, the greater the attraction between the nucleus and the electron. The effective charge increases across a period, in addition, the atomic radius decreases**
- **As we move down a group the distance from the nucleus increases and the attraction of the electrons for the nucleus decreases**

Which of the following elements has the lowest ionization energy? B, Al, C and Si

Probably Al. Its valence electrons have a higher principle quantum number, and are therefore further away from the nucleus, than C or B. Furthermore, its nucleus would have a lower effective nuclear charge than Si.

<u>Electron Affinities</u>

Atoms can also *gain electrons* to form negatively charged ions (*anions*)

The *electron affinity* is the energy change associated with an atom or ion in the *gas state* gaining an electron.

- ***For all positively charged ions, and most neutral atoms, energy is released when an electron is added***

$$Cl(g) + e^- \text{->} Cl^-(g) \ \Delta E = -328 \text{ kJ/mol}$$

Thus, we say that chlorine has an electron affinity of -328 kJ/mol.

The greater the attraction for the electron, the more exothermic the process

For anions and some neutral atoms, added an electron is an *endothermic* process, i.e. *work must be done to force an electron onto the atom*. This results in the formation of an *unstable anion*.

- **The halogens, which are one electron short of a completely filled *p* subshell have the greatest attraction for an electron (i.e. *the electron affinity* has the *largest negative magnitude*)**

  In adding an electron they achieve a stable electron configuration like the noble gases
- **The 2A and 8A groups have *filled subshells* (s, and p, respectively) and therefore, an additional electron must reside in a *higher energy orbital*. Adding an electron to these groups is an *endothermic* process**

Electron Affinities (kJ/mol)

1A	2A	3A	4A	5A	6A	7A	8A
H -73							He >0
Li -60	Be >0	B -27	C -122	N >0	O -141	F -328	Ne >0
Na -53	Mg >0	Al -43	Si -134	P -72	S -200	Cl -349	Ar >0
K -48	Ca -4	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr >0
Rb -47	Sr -11	In -30	Sn -107	Sb -103	Te -190	I -295	Xe >0

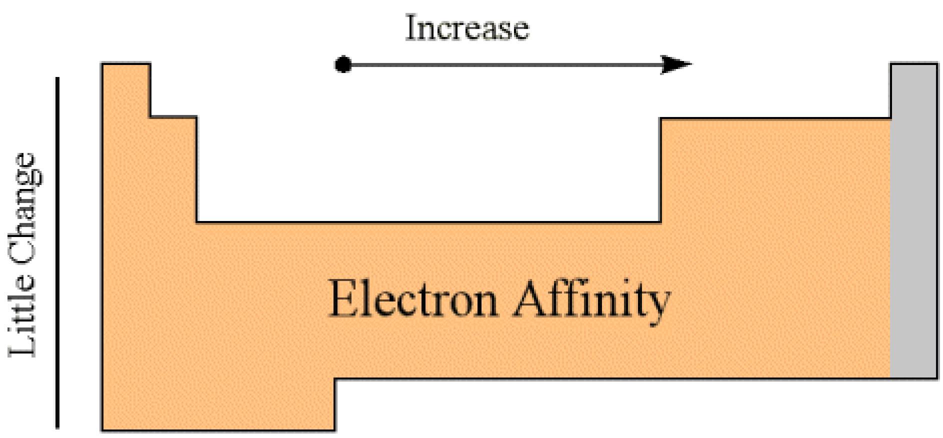
s subshell (1A–2A); *p* subshell (3A–8A)

The general trend is for the electron affinity to become increasingly negative (stronger binding of an electron) as we move across each period toward the halogens.

Electron affinities do not change much as we move down a group

- **The distance from the nucleus is increasing with greater n (less attraction) however,**
- **The electrons in the subshell are more diffuse, reducing electron-electron repulsions**

Element	Ion	E (kJ/mol)
F	F^-	-328
Cl	Cl^-	-349
Br	Br^-	-325
I	I^-	-295



General trends for the affinity of an element for the addition of an electron

Why are some substances chemically bonded molecules and others are an association of ions?

- **depends upon the electronic structures of the atoms**
- **nature of the chemical forces within the compounds**

<u>Chemical Bonding</u>

- **compounds are formed from chemically bound atoms or ions .**
- **bonding involves only the valence electrons .**

Chemical Bonding

- **Ionic Compounds**
  - **Ionic Radii .**
  - **Lattice Energy .**
- **Molecular Compounds**
  - **Covalent Bonds .**
  - **Bond Order .**
  - **Bond Strength .**
  - **Lewis Structures .**

A broad classification of chemical forces:

1. **Ionic bonds**
2. **Covalent bonds**
3. **Metallic bonds**

Ionic bonds - ***electrostatic forces that exist between ions of opposite charge***

An ionic bond is simply the electrostatic attraction between opposite charges.

Ions with charges Q1 and Q2:

The potential energy is given by: $$E \propto \frac{Q_1 Q_2}{d}$$

typically involves a metal with a nonmetal .

Covalent bonds

- **results from the sharing of electrons between two atoms**
- **typically involves one nonmetallic element with another**

Metallic bonds

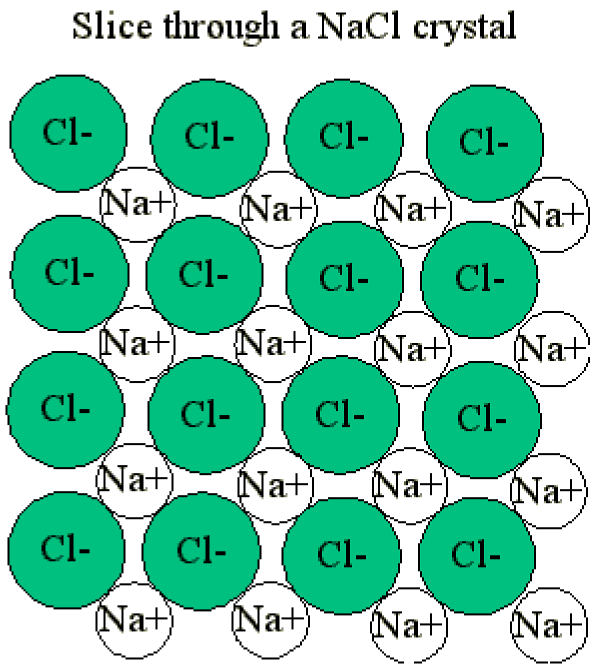
- **found in solid metals (copper, iron, aluminum)**
- **each metal bonded to several neighboring groups**
- **bonding electrons free to move throughout the 3-dimensional structure**

Ionic Bonding

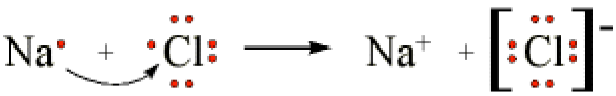
Sodium metal reacts with chlorine gas in a violently exothermic reaction to produce NaCl (composed of Na^+ and Cl^- ions):

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):



The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. This can be represented using *electron-dot symbols* (here we will consider one chlorine atom, rather than Cl_2):



The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an octet of electrons in its valence shell:

Na^+ $2s^2 2p^6$

Cl^- $3s^2 3p^6$

<u>Ionic Compounds</u>

ionic compounds consist of a lattice of positive and negative ions

Energetics of Ionic Bond Formation

The formation of ionic compounds (like the addition of sodium metal and chlorine gas to form NaCl) are usually *extremely exothermic*.

The loss of an electron from an element:

- **Always *endothermic* (takes energy to strip the e' from the atom)**
- **$Na(g) \rightarrow Na^{+}(g) + 1e^{-}$ $\Delta H = 496$ kJ/mol**
